Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 908

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June 2001

Submitted to
10th International Symposium on Corrosion in the Pulp and Paper Industry
(ISCPPI)
Helsinki, Finland
August 21-24, 2001

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Corrosivity of Black Liquors - Role of Wood Species Pulped

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Abstract

Black liquors after pulping different wood species can have very different corrosivity towards carbon steel equipment in pulp mills. Inorganic constituents of black liquor alone do not correlate well with the corrosivity of different black liquors. Organic constituents of the black liquor have been pointed out as determining its corrosivity. However, understanding of the role of organic constituents of black liquors individually and collectively in their corrosivity is generally lacking. The objective of this study was to determine the effect of five selected wood species on the corrosivity of black liquors with otherwise similar inorganic composition. The role of black liquor constituents like catechol, whose presence in black liquors has been associated with an increase in corrosion of carbon steel in black liquors, was also studied. Results from electrochemical tests point to the mechanisms by which catechols may participate in the accelerated corrosion of carbon steels. This study demonstrates the role of organic constituents of the black liquor in determining its corrosivity. Results from this study also confirm that correlation between the major inorganic constituents of the black liquor and the corrosion rate of steel alloys in these liquors is very poor.

Keywords: Black liquor, corrosivity, softwood, hardwood, digester, wood extractives, organic constituents, inorganic constituents, wood species

INTRODUCTION

The rate of corrosion for the equipment that comes in contact with black liquor varies considerably from one mill to other and within the same mill with changes in pulping parameters or wood species. Corrosivity of black liquors depends upon variables like temperature, flow rate, solids content, and chemical composition. Black liquor consists of residual inorganic chemicals after pulping, numerous organic constituents of wood, and other chemical species produced during the pulping process. Composition of black liquor varies with changes in chemical charge, cooking parameters, and wood species pulped. The major inorganic species in black liquor are sodium sulfide, sulfate, sodium thiosulfate, sodium carbonate, and sodium hydroxide. Sodium chloride may also be present as an impurity that can either originate from the water supply and/or from the wood chips. Therefore, the organic content of the black liquor largely depends on the wood species pulped and on the cooking process used.

The role of inorganic species in corrosivity of white and green liquors has been studied and reviewed by various researchers [1-6]. However, for the black liquors, a number of studies [7-17, 24] have shown that the corrosion rates of carbon steel equipment do not correlate with their inorganic composition. There are clear indications that organic constituents of black liquor play an important role in determining its corrosivity. However, there are literally hundreds of organic compounds detected in black liquors and they vary from wood species to wood species. For birch kraft black liquor, Niemela [18] discovered around 600 compounds but could only identify ~350 organic compounds using gas-liquid chromatography and mass spectrometry (GLC-MS). The role of wood extractives and other organic constituents of black liquor in the corrosion of pulping equipment is not very well understood.

Wensley [13] tested liquors from mills using hardwood and softwood and reported that the extraction liquors from softwood species were considerably more aggressive than hardwood extraction liquors. It was also reported that rates of corrosion did not correlate with the inorganic composition of tested liquors. Wood species (organic constituents and byproducts) seemed to have a significant influence on the corrosion behavior of carbon steel in different liquors. Kelly, et al., [15] analyzed the corrosivity dependence of various digester liquors on their solids contents, sulfides, sulfates, thiosulfates, and chloride concentrations and reported a significant variation in the corrosivity of different liquors.

The organic species in black liquor contain the degradation products of wood and include a variety of organic acids, fatty acids, and aliphatic sulfur compounds (such as dimethylsulfide). In addition to these organics, other wood extractives such as turpenes, resins, and phenols are also present. A number of compounds like thujaplicins, catechols, pyrogallol, pinene, and taxifolin, which are found in different wood species, have been pointed out as corrosive agents [9, 15-17].

MacLean and Gardner [9] reported that the life of a digester in a mill used exclusively for pulping western red-cedar (*Thuja plicata,* was half the life of other digesters used for western hemlock (*Tsuga heterophylla*) and Douglas-fir (*Pseudotsuga menziesii*). Results from experimental cooks showed that western red-cedar and Douglas-fir caused rapid attack on mild steel (50 to 60 mils per year) and the black liquor from western red-cedar was 50 to 60% more corrosive than that from Douglas-fir [9]. Western hemlock was reported to be relatively noncorrosive. MacLean and Gardner [9] concluded that the accelerated corrosion during pulping of western red-cedar in the areas which come in contact with the black liquor is caused by the presence of polyphenols of a catechol nature in the black liquors from western red-cedar. It is significant that 1-2-dihydroxybenzene compounds, such as catechol, the 1,2,3-trihydroxybenzene (pyrogallol), and their derivatives, cause active corrosion of carbon steels during alkaline pulping. Derivatives of catechol, e.g., catechin, queracetin, dihydroqueracetin, and derivatives of pyrogallol, e.g., gallic acid, allagic acid, gallotanins, and ellagitannins, occur widely in plants and as components of extractives of many pulpwoods and their barks [20]. Relative concentrations of these compounds in a given wood species may affect the relative corrosivity of its black liquor.

Niemela [19] identified 14 different catechols in pine kraft liquor. The most abundant compound was catechol (1,2-dihydroxybenzene), which was present in relatively high amounts (60-64 mg/liter) after the heating-up period, whereas only traces of other catechols and their derivatives could be detected after 165 minutes of cooking. Most of the catechols are formed by demethylation of their corresponding guaiacil structures, although the easy liberation of native catechol structures in lignin and aromatization reactions of carbohydrates also contribute to their formation during the pulping process. Investigators have confirmed that catechol and its derivatives can be formed from carbohydrates under alkaline conditions [19]. However, the fragmentation and recombination reactions required for the formation of catechols from carbohydrates are not well understood.

Kannan, et al., [17] measured the corrosivity of synthetic black liquor prepared with a set of 23 chemicals on A283 carbon steel samples. The results indicated that sodium sulfite, abietic acid, dimethyl sulfide, pinene, sodium thiosulfate, and pyrogallol are the chemicals that most contributed to the corrosion of A283 carbon steel in synthetic liquor. High concentrations of catechols (10g/L) were found to inhibit passivation due to their ability to form metal complexes with iron and their ability to destabilize iron oxides [4, 16].

Certain wood species contain other compounds that are known to increase the corrosivity of black liquors. Heartwood in Eucalyptus species contains appreciable amounts of acids, and the pH values of Eucalyptus wood extracts have been found to be around 2.5 and lower [20]. Although acetic and formic acids are known to be present in the Eucalyptus heartwood, the extent to which they contribute to acidity is not known. These acids are volatile weak acids and like tropolones can only cause corrosion in the liquid region of digesters before the chips are covered with alkaline pulping liquor [9, 20]; nevertheless, these acids can participate in the condensed vapor region of digesters or other black liquor handling equipment. However, if wet chips adhere and are isolated on digester walls, then it may be possible to get local pHs lower than the bulk mixtures.

Corrosivity of black liquors may also be affected by the inhibiting properties of certain organic compounds. Various degradation products of lignin may also inhibit corrosion. Tannin has been reported to form an organo-metallic compound with iron in alkaline solutions [21]. Alkali metal tannates act as corrosion inhibitors for carbon steels [22] and their formation may decrease corrosivity of black liquors. Tannins are also known to protect ferrous alloys from atmospheric as well as underground corrosion [23].

It is difficult to compare corrosivity of black liquors taken from different mills because it is difficult to separate out the effects of pulping conditions or inorganic constituents of black liquor from the effect of organic constituents on overall corrosivity of black liquors. The present study was aimed at establishing the relative corrosion susceptibility of carbon steels and other alloys in black liquors from different wood species, which were pulped in white liquor with the same composition under similar cooking conditions, leaving similar amounts of residual inorganic chemicals in resulting black liquors [24]. This is an initial effort in defining the role of wood species on determining the overall liquor corrosivity of black liquors.

Experimental Procedure

Five wood species commonly used for papermaking were selected from different regions of the United States. The species' scientific name and general location are indicated in Table I.

Table I. Wood species, type, and localization region in the U.S.

Common Name	Scientific Name	Type	U.S. Region
Douglas-fir	*Pseudotsuga taxifolia*	Softwood	Northwest
Loblolly pine	*Pinus taeda*	Softwood	Southeast
Cottonwood	*Populus deltoides*	Hardwood	Southeast
Sweetgum	*Liquidambar styraciflua*	Hardwood	South Central
Willow Oak	*Quercus phellos*	Hardwood	South

Wood chips from different species were cooked individually under conventional kraft pulping conditions in a laboratory digester, and the black liquor was extracted. One-and-a-half kilograms of oven-dry chips of a given species were cooked in a white liquor with composition given in Table IV. Pulping conditions used in this study have been described in detail elsewhere [24].

Five materials of construction, one carbon steel (A 516-G70), two austenitic stainless steels (SS316, SS304), and two duplex stainless steels (2304, 2205), were selected for this study. These materials are used in the construction of batch and continuous digesters and other black liquor handling equipment throughout the industry. Composition of these alloys is given in Table II. All the specimens were measured to calculate the exposed areas and the initial weight of each specimen was recorded using an analytical balance. Duplicate coupons were arranged in an insulated rack with a Teflon base. Crevice washers were used to construct these racks. The racks with duplicate metal coupons were placed in a 2205 stainless steel 3-

liter autoclave and submerged in the black liquor. The autoclaves were closed and heated with electric jackets and the specimens were exposed in the black liquor at 338°F (170°C) for 15 days, after which the coupons were removed, weighed, and examined for general and localized corrosion under the microscope.

Table II. Chemical composition of alloys used.

Alloy	Al	C	Cr	Cu	Fe	Mn	Mo	N	Ni	P	S	Si	V
A516	0.036	0.230	0.020	0.010	98.28	1.110	0.004	0.003	0.010	0.007	0.010	0.260	0.02
316		0.024	16.29		68.91	1.87	2.12	0.030	10.28	0.030	0.001	0.440	
304L		0.060	18.25	0.410	70.31	1.810	0.320	0.060	8.18	0.028	0.0003	0.570	
2205		0.010	22.45		66.38	1.66	3.19	0.153	5.57	0.024	0.006	0.56	
2304		<0.03	23.0		72.87	-	-	0.10	4.00	-	-	-	

The coupons were thoroughly cleaned with water, dried, and stored individually in closed plastic bags in a dessicator for further quantification. Weight of specimens was recorded before and after cleaning the surface with sandblast. Final weight, after sandblast, was used to calculate the corrosion rate. Before sandblasting, the specimens were examined for localized corrosion attack under crevice washers as well as on the general surface. Similar tests were also carried out in four synthetic liquors prepared in the laboratory. Composition of synthetic liquors is given in Table IV.

Potentiodynamic anodic polarization tests were also conducted in selected liquors using cylindrical specimens of carbon steel 1018 and 2205 duplex stainless steels. The main objective of anodic polarization tests was to understand the role of catechols, which have been pointed to as responsible for increasing the corrosivity of certain black liquors. Platinum foil was used as counter electrode whereas the potential was controlled using an external saturated calomel electrode (SCE) with luggin capillary. Test solution was purged with argon gas for an hour after which the anodic polarization tests were carried out. Fresh solution was used for each test. Test specimens were polished to one-micron finish and were cleaned and degreased just before the test. Potential scan rates of 0.5 mv/sec were used for the results discussed in this paper.

RESULTS AND DISCUSSION

Table III shows that the residual concentration of Na_2S, $Na_2S_2O_3$, and NaOH was similar for all black liquors tested in this study. Residual concentration of Na_2S and NaOH for all tested black liquors was between 4 and 5% of their initial concentration in the white liquor used for pulping. Composition of the white liquor and other synthetic liquors used in this study is listed in Table IV. Metal specimens were also tested in the white liquor and other synthetic liquors at 170°C.

Table III. Inorganic chemicals in black liquors before the corrosion test

	Chemical Composition of Black Liquor (in grams/liter)						Solids %
	$Na_2S_2O_3$	Na_2S	NaOH	NaCl	Na_2SO_4	Others	
Loblolly Pine	4.09	6.79	18.75	< 0.202	< 0.202	-	15.6
Douglas-fir	7.00	8.47	20.65	< 0.367	0.49	-	15.4
Douglas-fir-II	7.15	8.47	18.21	< 0.202	0.28	-	15.6
Sweetgum	7.36	10.22	16.72	< 0.204	0.20	-	14.4
Cottonwood	4.57	10.18	17.68	< 0.202	0.32	-	14.1
Willow Oak	8.77	8.47	12.86	< 0.194	0.22	-	17.8

Table IV. Composition of synthetic liquors tested

	Chemical Composition Synthetic Liquors (in grams/liter)					
	$Na_2S_2O_3$	Na_2S	NaOH	NaCl	Na_2SO_4	Others
Synthetic-I	4.09	6.79	18.75	0	0	-
Synthetic-VII *(Same as Synthetic-I)*	4.09	6.79	18.75	0	0	-
Synthetic-II	4.09	6.79	18.75	0	0	0.064 - Catechol
Synthetic-VI *(Same as Synthetic-II)*	4.09	6.79	18.75	0	0	0.064 - Catechol
Synthetic-III	-	-	-	-	-	5.0 - Catechol
Synthetic-V	4.09	6.79	18.75	0	0	6.4 - Catechol
White Liquor	-	149.8	450	-	-	-

Results from 15-day coupon exposure tests at 170°C in different black liquors and synthetic liquors are given in Table V. Corrosion rate for each material, listed in Table V, is an average value from duplicate test specimens. These results demonstrate that in general the carbon steel (516-Gr70) experiences significantly higher corrosion rates in corrosive black liquors and other liquors than the austenitic or duplex stainless steel samples.

A516-Gr70 coupons in softwood black liquors (loblolly pine and Douglas-fir) showed a very high corrosion rate of around 80 mpy. A black dusty film, which could be easily removed, covered these specimens. Corrosion was uniform and the attack was significantly less severe under the crevice washers compared to the general exposed surface of carbon steel coupons in softwood black liquors. Douglas-fir chips were pulped in two different batches and tests were conducted to check the reproducibility of our tests; the results shown in Table V for Douglas-fir-1 and Douglas-fir-II were very similar.

Carbon steel specimens tested in sweetgum and eastern cottonwood black liquors showed almost negligible corrosion. These specimens had brownish film on the surface but removal of the film exposed an unattacked surface underneath after 15 days of exposure at 170°C. However, in willow oak black liquor, which is also a hardwood, the corrosion rate of carbon steel specimens was significantly higher (~ 30 mpy) than that for the sweetgum and eastern cottonwood black liquors.

Table V. Average corrosion rate in mils per year (mpy)

Wood species	Corrosion rate in mils per year (mpy)				
	A516-Gr 70	**304**	**316**	**2205**	**2304**
Loblolly Pine	78.68	0.25	0.32	0.16	0.10
Douglas-fir-I	83.39	0.27	0.67	0.03	0.08
Douglas-fir-II	87.44	0.05	0.56	0.00	0.00
Sweetgum	0.00	0.10	0.05	0.17	0.11
E. Cottonwood	0.05	0.08	0.01	0.13	0.09
Willow Oak	32.61	0.15	0.06	0.06	0.04
Synthetic I*	0.18	0.12	0.21	0.21	0.14
Synthetic-VII* *(Same as Synthetic-I)*	0.92	0.45	0.51	0.48	0.65
Synthetic II**	0.30	0.18	0.10	0.03	0.04
Synthetic-VI** *(Same as Synthetic-II)*	1.02	0.93	2.04	0.73	1.32
Synthetic III***	2.43	0.18	0.10	0.14	0.13
Synthetic-V@	11.29	2.07	5.26	0.85	0.53
White Liquor	214.6	6.42	8.87	5.04	5.0

* $NaOH$, Na_2S, NaS_2O_3; ** $NaOH$, Na_2S, NaS_2O_3 + 64 mg/L Catechol; *** 5 g/L Catechol
@ $NaOH$, Na_2S, NaS_2O_3 + 6.4 g/L Catechol

Duplicate tests were conducted in the synthetic liquor (Synthetic-I and -VII) containing the same amounts of inorganic compounds as were analyzed in the loblolly pine black liquor in the present study. These tests were conducted to establish the effect of inorganic species alone on the corrosion of different alloys. Carbon steel specimens showed a black dark film after 15 days of exposure at 170°C but the corrosion rate was very low (less than 1 mpy) compared to the loblolly pine (~80 mpy). A very small amount of localized corrosion was observed under the crevice that could only be detected under an optical microscope. This clearly indicates that the inorganic components of an aggressive black liquor, loblolly pine in the present case, do not explain the overall corrosivity of black liquor.

Previous work by MacLean and Gardner [9] as well as by Kannan, et al., [4] has indicated that the catechols in liquor may be the reason for the aggressive nature of certain black liquors. To test that, we carried out other duplicate sets of tests where the specimens were exposed to Synthetic-II and -VI which were similar to the Synthetic-I but had catechol added to them. The amount of catechol was the same as was analyzed and reported by Niemela [19] for the loblolly pine black liquor (i.e., 0.064 grams/liter). Results in Table V indicate that the corrosion rate of carbon steel in Synthetic-II and Synthetic-VI liquors is slightly higher than that for the liquor without catechol (Synthetic-I and -VII). However, the differences were very small and the corrosion rate of carbon steel in Synthetic-II and VI was still very low (~1 mpy) compared to that for the loblolly pine black liquor (~80 mpy).

To check the corrosivity of catechols toward selected materials, tests were carried out in synthetic liquor (Synthetic-III) which contained 5 grams per liter of catechol in water, as shown in Table IV. Corrosion rate results, shown in Table V, indicate that the corrosion rates of carbon steel were very low compared to similar tests in softwood black liquors. Catechol concentration used in Synthetic-III was three orders higher (5g/L) than in loblolly pine black liquor (0.064 g/L) as reported by Niemela [19]. These results indicate that the catechol alone (even in concentrations much higher than that reported in loblolly pine black liquor), or the inorganic constituents of the black liquor alone, or the two in combination, do not explain why the softwood (loblolly pine) black liquor has such a high corrosivity. Another test was carried out in Synthetic-V liquor which was similar to Synthetic-II and -VI but had catechol concentration 100 times higher than Synthetic-II. Corrosion rates for carbon steel samples were higher with higher concentrations of catechols but were still much lower than the softwood black liquors. This clearly indicates that the individual corrosivity of any black liquor depends on more factors than were tested in this study.

There are indications that it is not just individual components but their interactions with each other that may be an important factor in overall corrosivity of black liquors. This is further shown by the results in Table VI, where different amounts of catechols were added to the noncorrosive black liquors (e. cottonwood and sweetgum). The results show that the addition of 64 mg/L of catechol to e. cottonwood black liquor increased the corrosion rate of carbon steel to 35 mpy. Similar addition in the Synthetic-II did not show any significant effect to increase the corrosivity. 27.5 g/L catechol was added to the sweetgum black liquor, which was noncorrosive to carbon steel on its own. The corrosion rate of carbon steel was 221 mpy, which was as high as the white liquor,or a corrosion rate almost 3 times higher than the softwood black liquors tested in this study. These results clearly indicate that the interaction of catechols with other organic constituents of black liquor is more complex. The sum total of the corrosion effect of individual constituents does not account for the collective effect of various liquor constituents.

Table VI. Effect of catechol addition on corrosivity of black liquors.

Black Liquor	**Catechol Added g/l**	Corrosion rate in mils per year (mpy)				
		A516-Gr 70	**304**	**316**	**2205**	**2304**
E. Cottonwood	**0.0**	0.05	0.08	0.01	0.13	0.09
E. Cottonwood	**0.064**	35.6	-	-	0.08	0.14
Sweetgum	**0.0**	0.00	0.10	0.05	0.17	0.11
Sweetgum	**27.5**	221.3	0.35	0.42	0.21	0.19

As expected, the general corrosion rates of austenitic as well as duplex stainless steel in all tested black liquors were very low (less than 0.7 mpy) compared to the carbon steels. However, the main objective of including stainless steel specimens in this study was to check localized corrosion susceptibility of different stainless steels in different black liquors. All tested specimens were observed under the optical microscope for localized attack. Table V summarizes these observations.

304 and 316 stainless steel coupons tested in the loblolly pine and Douglas-fir black liquor had a yellowish film on the surface. A slight localized corrosion attack was observed under the crevice washers for both austenitic stainless steels tested. 2205 duplex stainless steel specimens showed few corrosion pits on the surface and a minor crevice attack under the washers, as shown in Figure 3, but did not show significant uniform corrosion. However, 2304 SS did not show any signs of localized attack in softwood black liquor tests.

In Douglas-fir black liquor, 304 and 316 stainless steel specimens were covered with a dark brown film and exhibited significant crevice corrosion attack under washers for the 304 specimen, as shown in Figure 4. The 304L SS specimen exposed in Douglas-fir black liquor also had corrosion pits on the surface, as shown in Figure 5. 2205 and 2304 duplex stainless steels did not show any signs of localized corrosion attack in two separate tests done in Douglas-fir black liquors.

Austenitic as well as duplex stainless steel specimens had a light yellowish film on the surface; 2205 and 2304 were slightly stained. However there were no signs of crevice corrosion or pitting attack on any of the stainless steel specimens tested in sweetgum or e. cottonwood black liquors.

Table VII. Localized attack on different steel alloys.

Wood Species	**Type of localized corrosion attack**			
	304 SS	**316 SS**	**2205 DSS**	**2304 DSS**
Loblolly Pine	Crevice	Crevice	Crevice/ Pitting	-
Douglas-fir	Crevice/ Pitting	Crevice	-	-
Willow Oak	-	Crevice	-	-
Sweetgum	-	-	-	-
E. Cottonwood	-	-	-	-
Synthetic I & VII	Crevice/ Pitting	Crevice	Crevice	Crevice
Synthetic II & VI	Crevice	Crevice	Crevice/ Pitting	Crevice
Synthetic III	-	-	-	-
Synthetic-V	Crevice	Crevice	Crevice/ Pitting	Crevice
White Liquor	Crevice and Stress Corrosion Cracking	Stress Corrosion Cracking	Crevice/ Pitting	Crevice

Minor crevice corrosion was noticed on 316L specimens tested in willow oak black liquor. Willow oak black liquor was also the most corrosive to the carbon steel among hardwood liquors, as shown in Table V. However, 304L or duplex stainless steel specimens did not show any signs of localized attack in willow oak black liquor.

Tests in Synthetic-I and -II liquors produced a brownish film on the surface of 304 and 316 stainless steel coupons, whereas duplex stainless steel specimens had a yellowish film on the surface. Crevice corrosion was observed on all stainless steel specimens tested in synthetic-I and Synthetic-II liquors. Dispersed pits were also observed on the surface of 2205 duplex stainless steel specimens.

The Synthetic-II liquor containing 0.064 g/L of catechol did not appear to be significantly aggressive towards different alloys. Corrosion rates of A516-Gr70 and 304L SS were 0.3 and 0.18 mpy, respectively. MacLean and Gardner [9] showed that addition of 4.2 g/L of catechol to a 20 g/L NaOH solution increased the corrosion rate of carbon steel to 48 mpy compared to only 0.5 mpy for the solution without catechol. However, the concentration of catechol in our tests was much lower than that used by MacLean and Gardner. Significantly higher concentrations of catechol were also used in studies by Kannan and Kelly [4] or Tonsi-Eldakar and McGlynn [10,11] compared to the amount of catechol in the Synthetic-II liquor used in the present study, which was based on the amount of catechol identified in pine kraft black liquors using GLC-MS studies (60 mg/L) [19].

Specimens tested in Synthetic-III liquor, which only had 5 g/L of catechol in it, did not show any signs of uniform or localized attack on any stainless steel specimens. These results indicate that catechol in concentrations indicated by Niemela [19] for loblolly pine black liquor alone do not sufficiently explain the higher corrosivity of this softwood black liquor.

Duplex stainless steels (2205 and 2304) with their higher chromium content did not exhibit signs of localized attack in tested black liquors, except for the minor crevice attack of 2205 duplex stainless steel specimens in loblolly pine black liquor. However, all stainless steel specimens tested in synthetic liquors, Synthetic-I and Synthetic-II, showed crevice attack as well as dispersed pitting attack on the 2205 SS. Synthetic-I and -II liquors contained the same amounts of inorganics as analyzed in loblolly pine black liquor and were very similar to all other black liquors tested in the present study. This indicates that certain constituents of black liquors also protect stainless steels from localized corrosion attack, whereas in softwood and willow oak black liquors there are other constituents which cause higher corrosion rates for the carbon steel specimens.

Other major organic constituents of the black liquors should also be investigated systematically to understand the role of individual organics and their collective effect through chemical interactions with one another in determining the overall corrosivity of different black liquors.

Role of Catechols in Carbon Steel Corrosion

Potentiodynamic polarization results for carbon steel in different synthetic liquors are shown in Figure 1. Synthetic-I liquor was the baseline for this study and then different amounts of catechols were added to the baseline solution. As can be seen from Figure 1, the critical current density for carbon steel increased by over two orders of magnitude with an increase in catechols from 0.05 g/liter to 50 g/liter. This shows that the passive film formation becomes more difficult in the presence of catechols. This can be explained by tendency of catechols to complex with Fe^{2+} ions thus making it difficult to form the passive film during the anodic polarization test. The second effect of the addition of catechols was in decreasing the passivation potential zone with an increase in catechol concentrations. Wensley [13] reported that the carbon steels exhibit active, passive, and transpassive corrosion behavior in digester liquors, but the potential range for the passive region was very small for the softwood liquors compared to the hardwood liquors. Higher concentration of chemicals like catechols, which are generally found in loblolly pine black liquors and other softwoods, may be responsible for the decrease in passive potential region for the carbon steel, as shown in Figure 1.

Although different di- and trihydroxybenzenes (guaiacol, resocinol, catechol, pyrogallol) increase the corrosion potential of steel, the magnitude of the effect depends on their chemical structure and concentration. This is what was found in the coupon exposure tests as well as in the potentiodynamic polarization tests with catechols (pyrogallol) addition.

Similar polarization tests with 2205, shown in Figure 2, did not show any effect of catechol addition on polarization behavior. This is due to the fact that passivation for the chromium-containing alloys depends predominantly on the Cr^{+3} ions which do not complex with catechols and therefore do not experience an increase in corrosion rate in the presence of catechols.

Limited polarization tests were also carried out in black liquors, shown in Figure 3. These tests indicate that the effect of catechol in increasing the critical current density for carbon steel is similar to Synthetic-I solution. However, more systematic work is required to study the effect of catechols on different black liquors. Limited polarization tests clearly indicate that the catechols can increase the corrosivity of liquors towards carbon steels. Although catechols increase the corrosivity of black liquors, other organic constituents may directly or indirectly play a significant role in determining the overall corrosivity of black liquors from different wood species.

CONCLUSIONS

1) Results from the present study clearly indicate that organic constituents play a very important role in the overall corrosivity of black liquors.

2) Black liquors from loblolly pine and Douglas-fir (softwoods), produced by kraft process, exhibited corrosion of carbon steel at rates higher than 78 mpy, whereas black liquors from e. cottonwood and sweetgum (hardwood) black liquors caused almost negligible corrosion under otherwise similar testing conditions. However, black liquor from willow oak, which is also a hardwood, caused carbon steel to corrode at a rate of 33 mpy.

3) Liquors that cause high corrosivity towards carbon steel (i.e., Douglas-fir, loblolly pine, and willow oak) generally also cause localized attacks on 304L and 316 austenitic stainless steels.

4) Duplex stainless steel specimens in general have performed very well in all tested black liquors.

5) Addition of catechols do not increase corrosivity of an inorganic liquor significantly. However, in the black liquors, an addition of catechols have a very significant effect on increased liquor corrosivity

6) Anodic polarization results suggest that an increase in catechol concentration makes passive film development more difficult and decreases the passivation potential in both synthetic inorganic liquor and black liiquors.

7) Other major organic constituents of the black liquors need to be investigated systematically to understand their individual role as well as their collective effect through chemical interactions with one another in determining the overall corrosivity of different black liquors.

ACKNOWLEDGEMENTS

The authors wish to express special thanks to Blair Carter for his help in pulping. We greatly appreciate the help of Greg Makar, Steve Lukezich, and Margaret Gorog in providing chips from identified wood species for this study.

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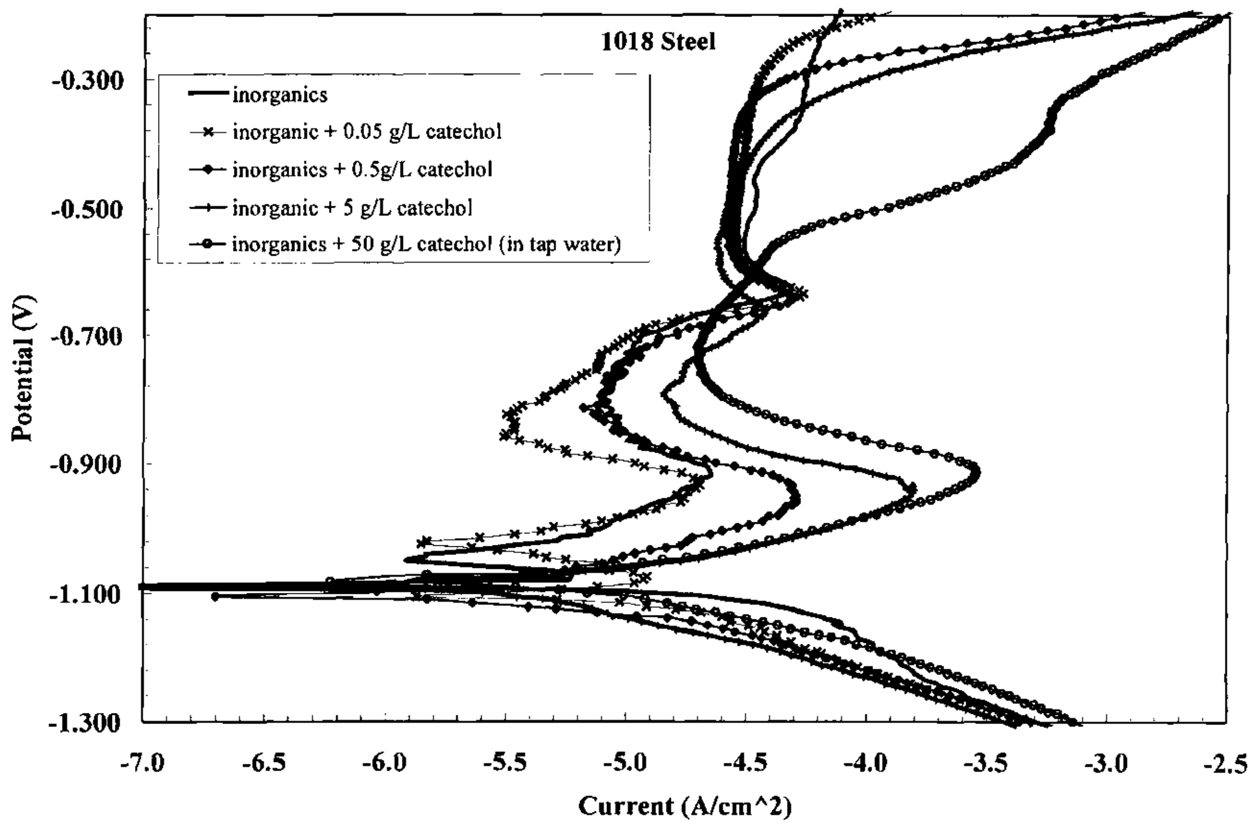

Figure 1. Anodic polarization behavior of carbon steel in different synthetic liquors.

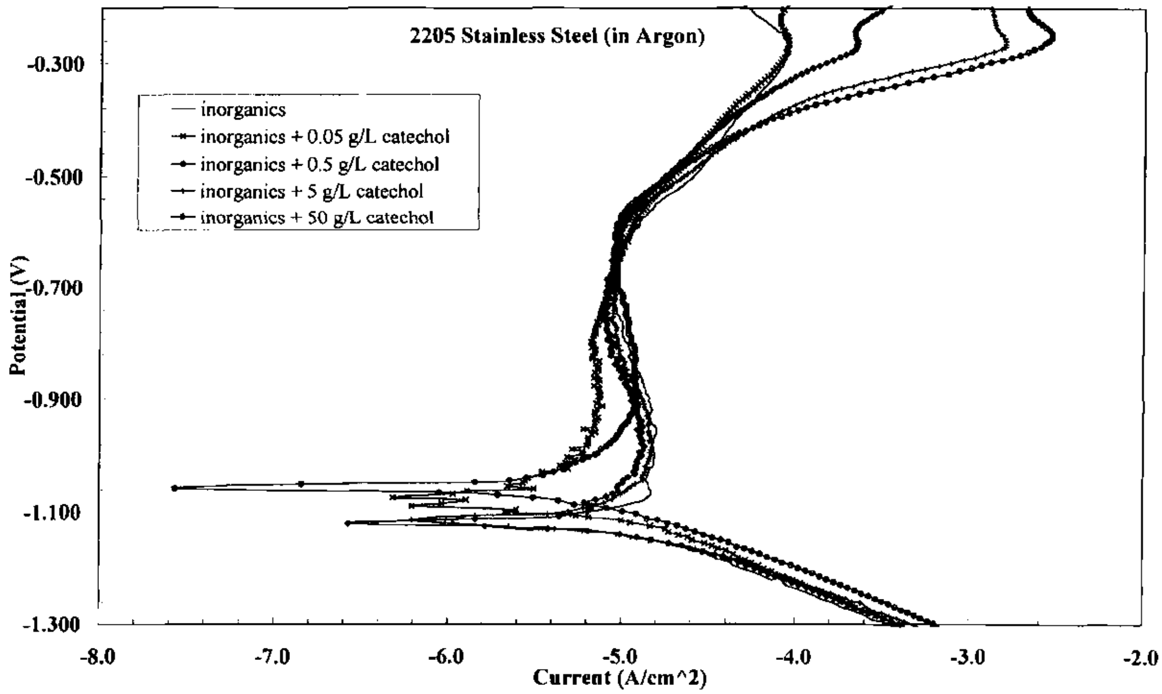

Figure 2. Anodic polarization behavior of 2205 duplex stainless steel in different synthetic liquors.

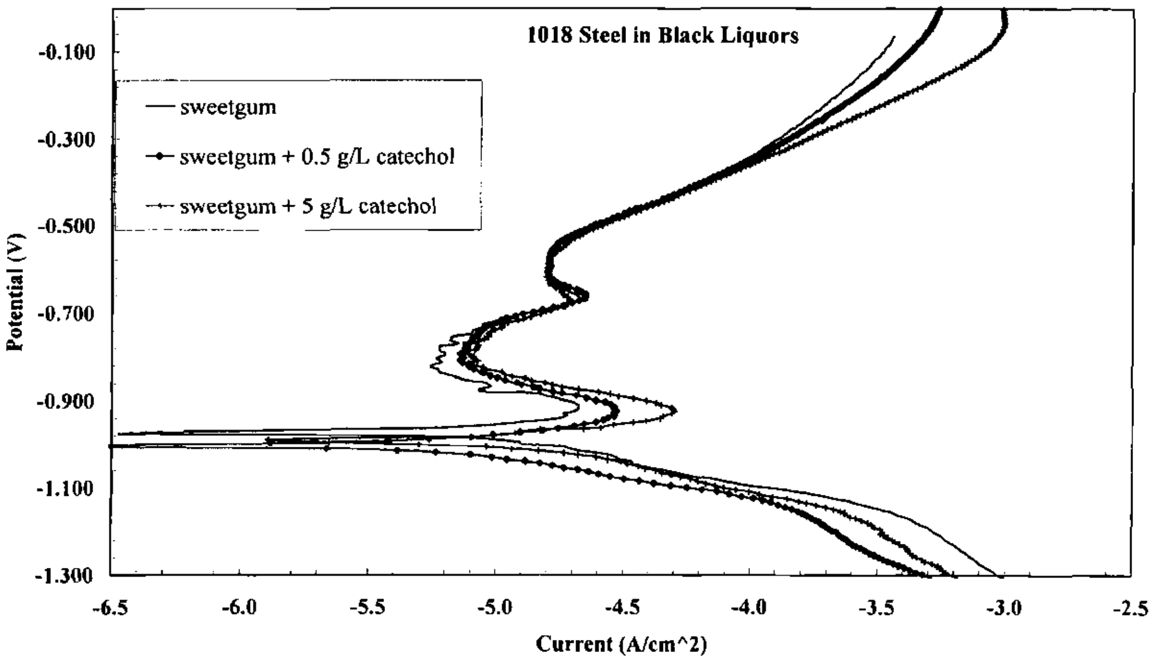

Figure 3. Anodic polarization behavior of carbon steel in sweetgum black liquor with and without addition of catechol.